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OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS  
REPORT

for

Grant N000-14-88-K-0389  
R&T Code: B 41C002DAR 01  
B 41C002DAR 02

A LIGHTWEIGHT SOLID POLYMER ELECTROLYTE  
FUEL CELL WITH STACK POWER DENSITY OF  
3kW/lb (7 kW/kg).

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**PART 1**

- a. **Papers Submitted to Refereed Journals (and not yet published):** None
- b. **Papers Published in Refereed Journals:** None
- c. **Books (and sections thereof) Submitted for Publication:** None
- d. **Books (and sections thereof) Published:** None
- e. **Technical Reports Published and Papers Published in Non Refereed Journals:** None
- f. **Patents Filed:** A. J. Appleby, "Improved Fuel Cell With Solid Organic Electrolyte", - (Invention Disclosure, 12-26-88; Patent to be filed)
- g. **Patents Granted:** None
- h. **Invited Presentations at Topical or Scientific/Technical Society Conferences:**
  - (i) "Recent Advances in Solid Polymer Electrolyte Fuel Cell Technology with Low Platinum Loading Electrodes", S. Srinivasan, D.J. Manko, H. Koch, M.A. Enayetullah, and A.J. Appleby. Paper Presented at the Second Space Electrochemical Research and Technology (SERT) Conference, NASA Lewis Research Center, Cleveland, OH April 1989. Paper to be presented at the 24th IECEC, Crystal City, Washington, D.C. August 1989. Proceedings to be published as a Special Issue of J. Power Sources.
  - (ii) "The Role of Electrode Kinetics and Electrochemical Engineering in Fuel Cell Research and Developments", S. Srinivasan. Paper Presented at the Annual Meeting of South Texas Local Section of Electrochemical Society, College Station, TX March 1988.

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- i. **Contributed Presentations at Topical or Scientific/Technical Society Conferences:**
- (i) "Alternate Methods for Platinum Localization in Electrodes to Attain High Power Densities in Solid Polymer Electrolyte Fuel Cells", M.A. Enayetullah, E. A. Ticianelli, D. J. Manko, S. Srinivasan and A. J. Appleby. Paper presented at the 175th Meeting of the Electrochemical Society, Los Angeles, CA May 1989.
  - (ii) "Investigations of Electrode Kinetics of Processes in Solid Polymer Electrolyte Fuel Cells Using AC Impedance Techniques", K.A. Murugesamoorthi, E.A. Ticianelli, S. Srinivasan, and A.J. Appleby. Presented in the ECS Meeting, Los Angeles, May 1989.
  - (iii) "Progress in High Power Density Fuel Cells", S. Srinivasan and E.A. Ticianelli. Paper presented at the 174th Meeting of the Electrochemical Society, Chicago, IL, October 1988.
- j. **Honors/Awards/Prizes: None**
- k. **Number of Graduate Students Receiving Full or Partial Support on ONR Grant or Contract: one**
- l. **Number of Postdoctoral Fellows Receiving Full or Partial Support on ONR Grant or Contract: one**

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**(continuation)**

**PART II**

- a. Principal Investigator: Dr. A. John Appleby**
- b. Cognizant ONR Scientific Officer: Dr. Robert Nowak**
- c. Current telephone number: (202) 696-4409**
- d. Brief description of the Project:**

The aim of the project is to develop the lightweight solid polymer electrolyte fuel cell technology for attaining high power density (stack power density of ~7 kW/kg). In order to achieve this goal, the objectives of the research are:

- (i) Investigation of the physiochemical properties of various solid polymer electrolytes and electrode kinetics at Pt/solid polymer electrolyte interfaces to attain maximum fuel cell performance;
- (ii) Optimization of low and high Pt loading gas diffusion electrode structures, membrane thickness, and of electrode-membrane bonding to obtain the most effective catalyst-membrane interface;
- (iii) Mathematical modeling of electrochemical, mass transfer and heating characteristics associated with cell operation to optimize fuel cell performance, with the aim of producing a stack capable of stated power density (7 kW/kg).

The work proposed, consists of three tasks:

- (i) Identifying the most suitable solid polymer electrolyte and optimizing the membrane thickness so as to minimize cell resistance and hence, maximize power density,
- (ii) Optimizing solid polymer-catalyst bonding to obtain the most effective catalyst-electrolyte interface hence, maximizing catalyst utilization, and
- (iii) Mathematical modeling of heat and mass transfer associated with cell cooling so as to optimize cell performance.

**e. Significant Results During Last Year:**

Attainment of high power densities has been demonstrated in single cells ( $5\text{ cm}^2$ ) with low ( $0.40\text{ mg/cm}^2$ ) platinum loading electrodes. These electrodes (Prototech, 20%Pt/C) were modified by (a) impregnation of Nafion and (b) localization of a thin layer of Pt ( $0.05\text{ mg/cm}^2$ ) on the active surface. Chemical and electrochemical deposition have been found to be viable alternate methods to sputtering one for platinum localization. The role of type as well as of thickness of the polymer membrane on fuel cell performance has been established; thinner the membrane better is the performance. The best performance ( $2\text{ A/cm}^2$  at  $0.62\text{ V}$ ) was obtained in single cells with Pt sputtered electrodes and Dow polymer membrane (thickness:  $125\text{ }\mu\text{m}$ ).

Preliminary thermal and material weight analysis indicates that cell cooling can be accomplished by high pressure recirculation of reactant gases.

**f. Brief Summary of Plans for Next Year's Work:**

The work planned for the next year is outlined as follows:

- (i) Electrodes with (a) high Pt loading, (b) new catalyst material (e.g., alloy catalysts) will be investigated in high-pressure single cell experiments,
- (ii) Cells with new polymer membranes (Dow, Ashahi) of different equivalent weights will be investigated.
- (iii) The  $5\text{ cm}^2$  single cell will be scaled-up to  $50\text{ cm}^2$  - cell to demonstrate similar performance level. Further, a 3 to 5 single cell stack will be assembled and attempts will be made to demonstrate the attainment of high power densities corresponding to the performance of  $50\text{ cm}^2$  cells.
- (iv) Mathematical model will be developed in order to address the problems of mass transfer, flow-field geometry, and heat transfer associated with water management cell cooling to optimize the multi-cell stack performance. These models will be further developed to address the problems of heat and water management for a specific cell design.

**g. List of Names of Graduate Students and Postdoctoral(s) Currently Working on the Project:**

- 1) Mr. Arvind Parthasarathy (Graduate-student)
- 2) Dr. Mohammad Enayetullah (Postdoctoral Research Associate)

**h. Technical Reports Submitted to ONR During the Past Year:**

Three (3) Quarterly Reports submitted to DARPA/ONR

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(continuation)

**PART III**

- a.     **An introductory "viewgraph":** (See viewgraph 1)
- b.     **A figure:** (See viewgraph 2)
- c.     **A concluding "viewgraph":** (See viewgraph 3)
- d.     **A paragraph of explanatory text:** (See page 10)

# A LIGHTWEIGHT SOLID POLYMER ELECTROLYTE FUEL CELL WITH STACK POWER DENSITY OF 3 kW/lb (7 kW/kg)

TEXAS A&M UNIVERSITY SYSTEM

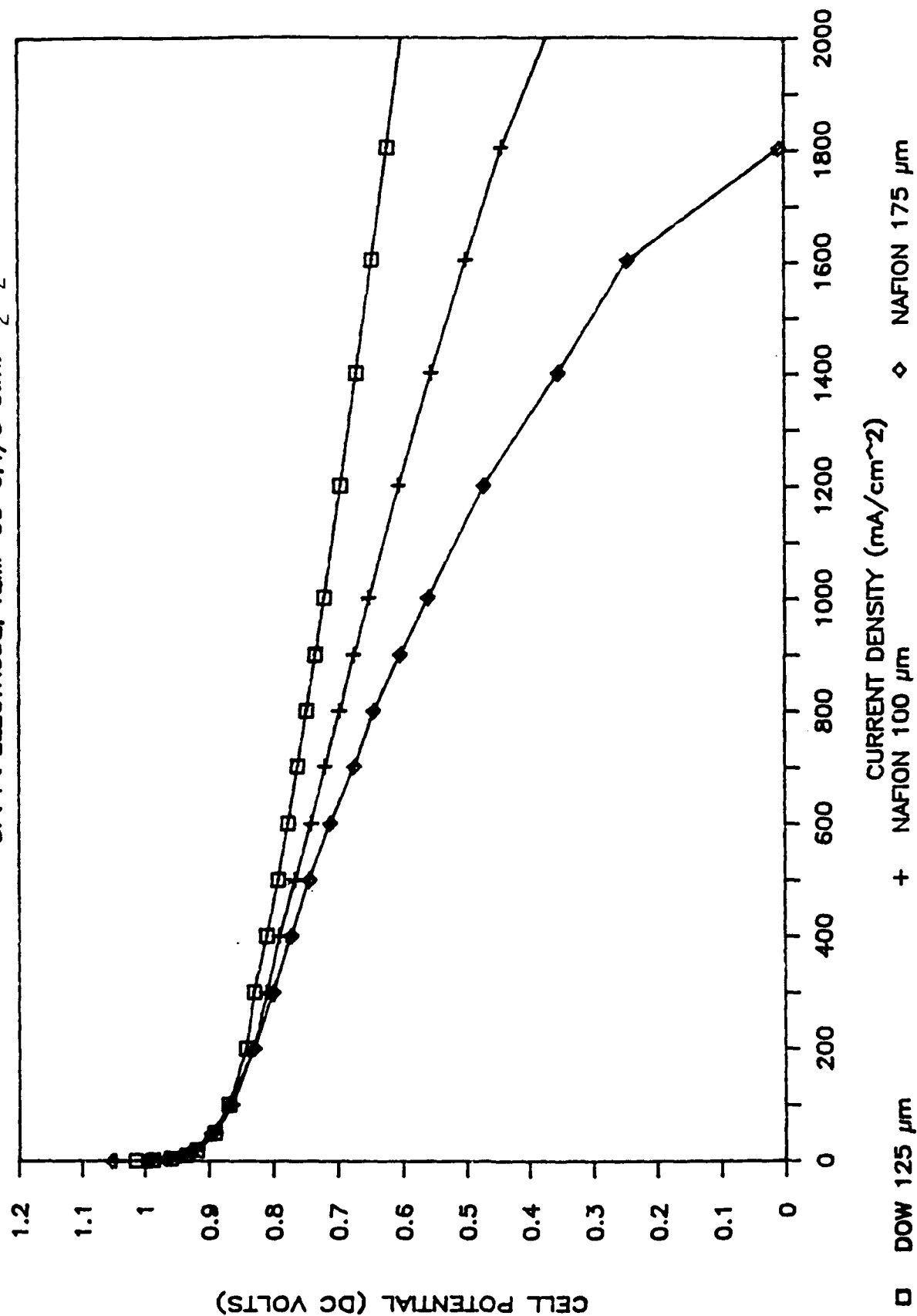
A.J. APPLEBY, S. SRINIVASAN, E.A. TICIANELLI, M.A. ENAYETULLAH, D.J. MANKO,  
H.KOCH, D.H. SWAN, A. PARTHASARATHY, C.R. MARTIN AND R.E. WHITE

## OBJECTIVES

- Investigations of physico-chemical properties of various solid polymer electrolytes and electrode kinetics at Pt/solid polymer electrolyte interfaces
- Optimization of low and high Pt-loading gas diffusion electrode conditions, structures, membrane bonding to obtain most effective electrolyte catalyst membrane interface and hence attain maximum fuel cell performance
- Mathematical modeling of electrochemical, mass transfer and heat generation characteristics associated with cell operation to optimize fuel cell thermal and water management.

## APPROACHES

- Develop micro-electrode technique to investigate electrode kinetics at Pt/solid polymer electrolyte interfaces and determine mass transport parameters of reactants
- Develop methods, alternative to sputter deposition to localize platinum near front surface of electrode
- Optimize <sup>(1)</sup> amount of proton conductor impregnation into porous gas diffusion electrodes and <sup>(2)</sup> Hot pressing of electrodes to membranes
- Reduce ohmic overpotential in cell by using Dow thinner Nafion membranes and Dow membranes with better water retention characteristics
- Modeling to determine most efficient methods for performance, with aim of producing stack power density of 7 kW/kg

SP. Pt ELECTRODE, TEMP 95 °C./5 atm. ( $H_2/O_2$ )

Effects of type and thickness of polymer electrolyte membrane on the cell potential vs. current density plots for single cells using Pt-sputtered Prototech electrodes (20% Pt/C, 0.4 g/cm<sup>2</sup> Pt).



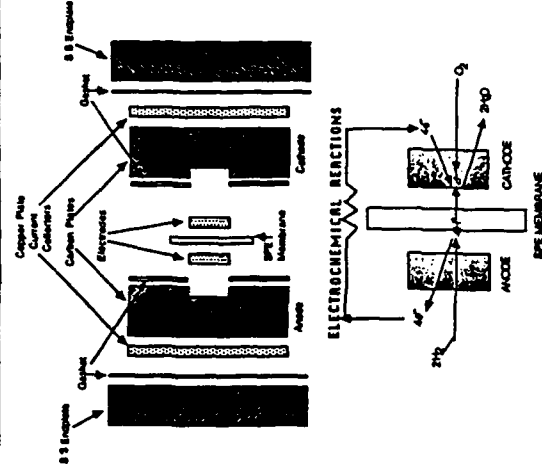
# A LIGHTWEIGHT SOLID POLYMER ELECTROLYTE FUEL CELL WITH STACK POWER DENSITY OF 3 kW/lb (7 kW/kg) (cont...)

TEXAS A&M UNIVERSITY SYSTEM

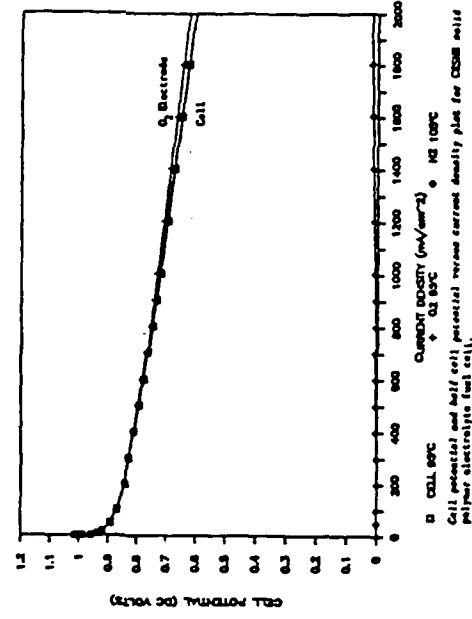
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## ACCOMPLISHMENTS TO DATE AND ANTICIPATED

- Single cells ( $5 + 50 \text{ cm}^2$ ) and test station designed and constructed for performance evaluation
- Developed chemical and electrochemical methods, as alternatives to sputter deposition for localization of platinum near front surface. Total platinum loading  $3.45 \text{ cm}^2$
- Optimized conditions for impregnation of proton conductor into electrodes and for hot pressing of electrodes into membranes
- High performance of single cells ( $\text{H}_2/\text{O}_2$ ) attained with low platinum loading electrodes ( $2 \text{ A/cm}^2$  at  $0.6 \text{ V}$ ) see Figure 2. Performance comparable to that obtained with high platinum loading electrodes
- Design and fabrication of multicell stack ( $50 \text{ cm}^2$ ) in progress
- Modeling studies commenced to determine most effective methods for heat and water removal
- Model will be checked with results of experimental work on multicell stack



Schematic of  $5 \text{ cm}^2$  single cell



The performances of solid polymer electrolyte fuel cells (electrode area: 5 cm<sup>2</sup>) were evaluated by recording their half/single cell potential vs. current density data. A schematic of the single cell assembly is shown in Viewgraph 3. Half and single cell potential vs. current density plots for a single cell using platinum-sputtered electrodes and Dow membrane are also shown in Viewgraph 3. This data represents the best performance (0.62 V at 2 A/cm<sup>2</sup>) attained in single cells with low platinum loading electrodes. The performance of this cell is compared with the performances of single cells using Nafion membranes of two different thicknesses in the figure in Viewgraph 2. It shows that the cell potential vs. current density plots almost overlap in the low current density region (say up to 50 mV). This means that the activation-controlled behaviour is unaffected by the characteristics of the membrane (Dow vs. Nafion, Nafion thick vs. thin). This result can be interpreted on the basis that the electrochemical reaction occurs to a large extent within the pores on the surfaces of the electrodes which are coated with Nafion in all the single cells. With increasing current density, the role of the membrane (type, thickness) is dominant and consequently the slopes of the linear region are different. One significant result is that the slope of the linear region in the cell with the Dow membrane is less than that in the cell with the Nafion membrane even though the thickness is greater in the former case (125  $\mu$ m vs. 100  $\mu$ m). This result may be rationalized on the basis that the Dow membrane has a higher specific conductivity than that of the Nafion membrane. Another interesting observation in Figure 1 is the departure the E-i plots at higher current densities; the cell with Nafion, 175  $\mu$ m and 100  $\mu$ m, shows departure whereas one with Dow, 125  $\mu$ m, does not. Such a departure from linearity at high current densities are generally attributed to mass transport limitations of reactants reaching the active sites in the electrode or of products away from the electrocatalytic sites. The electrode structures and conditions of humidification of reactant gases were identical in all the cells in the present investigations and hence there must be some other explanation for the mass transport limitations in the cells with thicker (175  $\mu$ m and 100  $\mu$ m) Nafion membrane. It is very likely that transport processes within the membrane can be rate-limiting. The transporting species are protons, which migrate from anode to cathode under the influence of the electric field, and water (estimated to be 3-6 molecules) which are carried with each proton. Due to the resulting concentration gradient of water in an operating cell, water molecules must diffuse back from the cathode to the anode. Mass transport limitation could occur due to any one or more of these processes.